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DOI: https://doi.org/10.1002/cssc.201900974

Preface to Special Issue of ChemSusChem—Water Splitting: From Theory to Practice

S. David Tilley,*[a] Annabella Selloni,*[b] and Takashi Hisatomi*[c]

[a] Prof. Dr. S. D. Tilley,
Department of Chemistry, University of Zurich
Winterthurerstrasse 190, 8057 Zurich (Switzerland)
E-mail: david.tilley@chem.uzh.ch

[b] Prof. Dr. A. Selloni
Department of Chemistry, Princeton University
Princeton, NJ 08544 (USA)
E-mail: aselloni@princeton.edu

[c] Dr. T. Hisatomi
Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University
4-17-1, Wakasato, Nagano City 380-8553 (Japan)
E-mail: hisatomi@shinshu-u.ac.jp

Abstract
In this Editorial, Guest Editors David Tilley, Annabella Selloni, and Takashi Hisatomi introduce the Special Issue of ChemSusChem on Water Splitting: From Theory to Practice. The significance and enormous challenges of sunlight-driven water splitting are reviewed and the contents of the contributions to the Special Issue are outlined.

Sunlight-driven water splitting has been studied actively for production of renewable solar hydrogen as a storable and transportable energy carrier. Hydrogen can also be used to fix carbon dioxide and nitrogen by catalytic processes to produce fuels and valuable chemicals.[1] Efficiency, scalability, and cost of water-splitting systems are essential factors for this scheme because of the low power density of solar energy (necessitating large-area devices), and the low price of fossil fuels as the market competitor. There are various visions on how practical solar hydrogen production via the water splitting reaction could come to be. For instance, it has been estimated that 10000 solar hydrogen production plants 25 km2 in size are needed to support one-third of our energy demand in 2050, even if a solar-to-hydrogen (STH) energy conversion efficiency of 10% is assumed.[2] A low cost of approximately 100 US dollars per square meter will also be needed to make this scheme economically feasible.[3]

To tackle this enormous challenge, a global scale collaboration encompassing several related scientific fields is required. In this Special Issue of ChemSusChem, we highlight that this large-scale collaboration is currently underway. In this collection of Minireviews, Full Papers, and Communications on topics ranging from fundamental theoretical studies all the way to large-scale (photo)electrode synthesis, researchers from around the world are bringing their expertise to bear on this important challenge. Herein, we summarize the contents of this Special Issue.

In recent years, theoretical studies based on density functional theory (DFT) have provided both detailed insights into the behavior of selected catalyst surfaces and predictions of new promising materials for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). For example, using the scheme of the computational hydrogen electrode to calculate the free-energy changes associated with the elementary steps of the HER/OER,[4] it is possible to determine the theoretical overpotential, which can then be used to estimate the relative performance of different materials. In this Special Issue, **di Valentin and co-workers** employed such an approach to investigate the OER activity of free-standing and Cu(111)-supported h-BN based 2D materials. Their results indicate that in general pristine and modified h-BN materials have either a large overpotential or require a large free energy for the last step of O_2 release, and therefore are not good electrocatalysts for water oxidation. However, rational engineering can significantly improve their performance, as demonstrated for a system composed by Cu tetramers trapped within large lattice defects in a h-BN layer supported on Cu(111), for which both the overpotential and the free-energy cost of O_2 release are found to be relatively low (~0.6 eV).

An important characteristic of many OER electrocatalysts is that they change their crystal structure, morphology and/or composition under operating conditions. Understanding these changes is essential for identifying the catalysts' active site and thus controlling their behavior. The Minireview by **Ye-Fei Li** addresses this issue and describes recent theoretical advances in the simulation of the morphology and structural evolution of OER catalysts. In this

Minireview, the author first illustrates the correlation between OER activity and morphology considering anatase TiO_2 nanoparticles as a model system. Next, focusing on manganese oxides, he demonstrates how calculations of the OER activity combined with global search algorithms of the crystal structure can provide insight into the active sites of the electrochemically induced δ-MnO_2 phase. Finally, he also shows how this approach can be extended to elucidate the structure of the complex heterointerfaces between oxides and sulfides, for example, CoS_2/CoOOH and NiS_2/NiOOH, that form on sulfide OER catalysts under operating conditions.

Many electrode materials for photoelectrochemical (PEC) water splitting typically require surface passivation with organic molecules for protection against photocorrosion. Surface functionalization with organic molecules is also used to tune the barrier height at the semiconductor–electrolyte interface or to 'sensitize' the semiconductor electrode so as to increase the absorption of visible light. In this Special Issue, the Minireview by **Iyer and co-workers** provides a theoretical perspective on these topics, specifically discussing how theoretical studies can yield "predictive insights and complement experimental investigations of functionalized photoelectrodes". The Minireview summarizes the background and relevant computational studies of the various aspects of molecular functionalization on different materials and also discusses future directions of computational modelling, stressing that novel multiscale approaches will be needed to advance the field.

Experimentally, researchers usually focus on one of the two water splitting reactions, either proton reduction to molecular hydrogen (HER) or water oxidation to oxygen (OER). The OER supplies the electrons for storage in the hydrogen fuel. Two Minireviews in this issue focus on photocathodes for hydrogen evolution. **Jang and Lee** give an up-to-date account on progress with p-type metal oxide semiconductor photocathodes, while **Yang and Moon** describe recent progress on Earth-abundant photocathodes for PEC water splitting. The coupling of molecular catalysts to light-absorbing semiconductor surfaces is being increasingly explored, and a third Minireview by **Morikawa and co-workers** summarizes the recent progress in molecular-catalyst-immobilized photocatalysts and photocathodes for proton reduction to hydrogen.

The efficient oxidation of water is a key challenge for the production of renewable fuels on a large scale. Three papers in this issue focus on molecular approaches to water oxidation. **Gimbert-SuriÇach and co-workers** report catalytic water oxidation with mononuclear ruthenium complexes bearing a 2,6 pyrindinedicarboxylato ligand, and **Yagi and co-workers** review recent progress in the coupling of such molecular catalysts to conducting surfaces, generating molecular-based anodes for the electro-oxidation of water. **Inoue and co-workers** demonstrate that aluminum porphyrins oxidize water to hydrogen peroxide in the presence of sodium carbonate. By generating a chemical with more value than oxygen at the anode, the overall economics of a solar fuel generator are improved.

Two further papers focus on inorganic thin films for water oxidation. Ni–Fe (oxy)hydroxide and Co–Fe (oxy)hydroxide materials are Earth-abundant materials that are highly active in alkaline media and have therefore been the subject of much research. The incorporation of Fe into Ni and Co (oxy)hydrox ides is important for the activity, although the details of the interaction of Fe with Ni or Co remain unclear. In a VIP paper in this issue, **Dau and co-workers** approach this issue by oxidizing NiFe alloys to generate highly active

electrocatalysts and then characterizing these electrodes with a range of X-ray techniques in combination with time-resolved spectro-electro chemistry, and the authors are able to shed light on the important role of Fe in these systems. **Xiang, Boettcher, and co workers** identify differing modes of Fe incorporation into $Co(Fe)O_xH_y$ thin films dependent on synthesis conditions, and find that the fabrication method has important implications on both the efficiency and stability of these electrodes.

Cobalt phosphides are another class of material that is under investigation for both the HER and OER reactions due to the high stability in both acidic and basic media. **Hou, Wang, and co-workers** describe a simple technique based on LiCl phase-transfer catalysis that generates highly active Co_2P nano sheets both for the OER in basic media (10 $mAcm^{-2}$ at an over potential of 0.28 V) as well as the HER in acidic media (10 $mAcm^{-2}$ at an overpotential of 0.238 V). By continuing to improve the overpotentials of these Earth-abundant catalysts, generating fuels from renewable energy will become increasingly attractive.

Regarding photo-oxidation of water, two papers report ad vances with the important photoanode material BiVO4. **Abdi, Wong, and co-workers** use a suite of techniques to provide insight into the origin of the improvement in the photocurrent when NiOx co-catalyst is deposited on BiVO4. **Stefik and co-workers** report a host–guest approach of atomic layer deposition (ALD)-fabricated $BiVO_4$ with optimized pore volumes that yield a new record for applied bias photon-to-charge efficiency with ALD-deposited photoanodes.

A very important challenge in semiconductor-based water splitting is the stability of the materials in contact with aqueous electrolytes under illumination. In this issue, **Nandjou and Haussener** develop a kinetic model to investigate the competition between photocorrosion and the reaction of interest (e.g., oxygen evolution). They demonstrate that it is important to consider not only thermodynamic factors when assessing the expected stability of semiconductor systems (especially with the incorporation of highly active co-catalysts on the surface). Depending on the rate constant for oxygen evolution vs. the activation barrier for the photocorrosion reactions, it is shown that thermodynamically corrodible materials can be stable anywhere from minutes to years.

Particulate photocatalyst systems can be spread over wide areas by potentially inexpensive processes. Development of photocatalytic systems highly active in water splitting under sunlight has a huge impact on the realization of practical solar to-fuel conversion processes. In reality, however, the demonstration of large-scale photocatalytic systems is yet to be realized, let alone commercialized processes, because of the lack of photocatalytic systems operating at appreciable efficiency and durability under natural sunlight. In fact, the STH efficiency of particulate photocatalyst systems is currently an order of magnitude lower than those of electrolyzers and PEC cells powered by photovoltaics. Consequently, technical challenges associated with scale-up have been overlooked. We still have to define visions toward practical processes although almost four decades have passed since the first reports of overall water split ting on particulate semiconductor photocatalysts. Nevertheless, recent remarkable improvement in the apparent quantum yield and the durability of photocatalysts in overall water split ting, and the progress in understanding of materials properties and dynamics of photoexcited carriers in catalyst/semiconductor composites, raise hopes that efficient sunlight-driven water splitting reaction could be realized. Therefore, it is timely to review the intensively studied potential photocatalysts and to highlight the emerging materials, systems,

and latest understanding on reaction processes to know the origin of the research on photocatalytic water splitting and for inspiration for future research.

This Special Issue covers three Minireviews on particulate photocatalysts, namely, sodium tantalate (**Onishi**), graphitic carbon nitride (**Hu and co-workers**), and anion-mixed materials (**Zhang and co-workers**). These materials have motivated the research field owing to their high reaction efficiency, a variety of applications under visible light, and intense visible light ab sorption ideal for effective harvesting of solar energy, respectively.

Understanding reaction properties of particulate photocatalyst systems is essential to rectify problems and upgrade the photocatalytic water splitting activity. However, the overall water-splitting reaction is complicated because both HER and OER occur simultaneously on particulate materials and is indeed difficult to achieve owing to a large increase of the Gibbs energy for the reaction (+ 237 kJ per mole of water at the standard condition at 298 K). Accordingly, sacrificial electron donors and acceptors are often employed to focus on the HER and OER activity of photocatalytic systems. Sacrificial electron donors (such as methanol, triethanolamine, and sodium sulfide/sulfite) consume photoexcited holes irreversibly and more efficiently than water. Thus, one can focus on reaction processes associated with HER driven by photoexcited electrons. Likewise, sacrificial electron acceptors (such as silver cation) can be used to discuss the oxygen evolution ability of photocatalysts. The activity of photocatalysts in overall water splitting and sacrificial hydrogen or oxygen evolution reactions may be governed by different factors, although investigation of photocatalytic systems using sacrificial reagents can provide a hint to efficiently utilize photoexcited carriers. For example, **Schmuki and co-workers** found that Ti^{3+} states in anatase generated under illumination in an aqueous methanolic solution promoted the HER based on electron paramagnetic resonance spectroscopy, reflectivity, and PEC techniques. **Chen, Xu, and co-workers** reported bifunctionality and strong interaction of platinum species deposited on carbon nitride by chemical reduction in the HER from aqueous triethanolamine solution. Metallic Pt0 and cationic Pt^{2+} species existed on carbon nitride with high dispersion and allowed for excellent hydrogen evolution activity at relatively low Pt loading. Notably, Pt^{2+} species prevented backward reactions of H2. In the overall water splitting reaction, **Yoshida and co-workers** identified similar roles of oxidized Pt species deposited on a CaTiO3 photocatalyst in water vapor splitting. The platinum species loaded by an impregnation method retained the oxidized form under photoirradiation and promoted hydrogen and oxygen production without promoting the reverse reaction. As for Z-scheme water splitting based on two-step excitation of photocatalysts, **Sun, Domen, and co-workers** studied powder suspension systems of $La_5Ti_2CuxAg_{1-x}S_5O_7$ materials with different Cu/Ag ratios combined with PtO_x-loaded WO_3 and I_3^-/I^- redox couple. The use of $La_5Ti_2AgS_5O_7$ led to the highest water splitting activity as opposed to the Z-scheme particulate sheets, and the difference in optimization strategies for Z-scheme water splitting were discussed.

The development and activation of photocatalytic materials with intense visible-light absorption has been an important task of sunlight-driven water splitting. **Kudo and co-workers** studied solid solutions of Cu_3VS_4 with Cu_3NbS_4 and Cu_3TaS_4 with band gap energies of 1.6–1.7 eV. Most solid solutions showed better activities in sacrificial H2 evolution under visible light irradiation than the original Cu_3MS_4 (M= V, Nb, Ta). It was also shown that these solid solutions functioned as photocathodes. $Cu_3Nb_{0.9}V_{0.1}S_4$ was identified as the best material

for photocatalytic and PEC applications and enabled PEC water split ting under simulated sunlight irradiation without an external bias when being combined with a CoO_x-loaded $BiVO_4$ photoanode.

Another important but mostly unconsidered subject is scale up. **Pokrant and co-workers** studied a scalable fabrication pro cess of particle-based photoanodes using $LaTiO_2N$. The primary issue was thus how to suppress the contact resistance for large-sized $LaTiO_2N$ photoanodes because small lab-scale NH_3 flowing furnaces were not applicable. By optimizing the fabrication steps based on scalable electrophoretic deposition, annealing in air, and dip coating, $LaTiO_2N$ photoanodes with decent activity were developed. Then, the electrode geometrical dimension was actually increased from 1 to 40 cm2 scale. However, the photoelectrode size was shown to affect the performance even on the 0.1 m scale because of lateral resistance in the conductive substrate. Their work represents a problem of scale up of water-splitting systems. On the other hand, **Amano and co-workers** studied unique PEC cells splitting moisture to omit processes associated with purification of feed water. The PEC cell was based on a macroporous titanianano tube array photoanodes and a proton exchange membrane. A surface coating of the photoanode with a solid-polymer electrolyte was shown to enhance the incident photon-to-current conversion efficiency markedly, indicating the importance of proton-coupled electron transfer for successful water split ting with this type of PEC cells.

Through this short introduction of the published works in this Special Issue of ChemSusChem, readers will find how broad and exciting the research topics of water splitting are and how large is the number of countries/regions that have been actively involved. We, the Guest Editors, appreciate contributions by the authors around the world and the support by the reviewers who critically evaluated the submitted works to guarantee the high level of science, as well as the editorial staff who directed the organization of this Special Issue. We hope that the reader will enjoy the contents and find positive inspiration for further progress.

Keywords: density, functional calculations, electrocatalysis,·photocatalysis, photoelectrochemistry, water splitting

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David Tilley received his PhD in Chemistry from the University of California, Berkeley under the supervision of Prof. Matthew Francis. After a post doctoral research stint at Princeton University with Prof. Erik Sorensen, he joined the laboratory of Prof. Michael Grätzel at the EPFL in Switzerland as a postdoctoral fellow to learn semiconductor-based photoelectrochemistry. He served as the group leader of the hydrogen subgroup of the Grätzel laboratory for 3 years, before taking up an Assistant Professorship at the University of Zurich, where he remains today. His research interests are thin film photoelectrochemical systems for water split ting and synthetic electrochemistry in general.

Annabella Selloni is David B. Jones Professor of Chemistry at the Depart ment of Chemistry of Princeton Univer sity. She received her Ph.D. from the Swiss Federal Institute of Technology (Lausanne, Switzerland), and before joining Princeton University she held positions at the University “La Sapien za” (Roma, Italy), at the International School for Advanced Studies (Trieste, Italy), and at the University of Geneva (Switzerland). Professor Selloni has co-authored more than 300 publications. Her research focuses on the theoretical modelling of surfaces and interfaces by first principles electronic structure calculations and ab initio molecular dynamics simulations. She is particularly interested in metal oxide surfaces and aqueous interfaces for application in photocatalysis and photovoltaics. She is a Fellow of the European Academy of Sciences (2016) and the American Physical Society (2008), and has been named an APS Outstanding Referee (2012).

Takashi Hisatomi received his Ph.D. in Engineering from the University of Tokyo under Prof. Dr Domen’s supervision in March 2010. He studied as a postdoctoral fellow in Laboratory of Photonics and Interfaces of Ecole Polytechnique Fédérale de Lausanne from April 2010 to March 2012. He moved to the University of Tokyo in April 2012 as a postdoctoral fellow and acquired a position of Assistant Professor in August 2012. He moved to Shinshu University as Associate Professor in April 2018. His major research interests are semiconductor photocatalysts and photoelectrodes for overall water splitting, kinetics and reaction selectivity of photoexcited carriers in semiconductors, and reaction systems and processes for renewable solar fuel production.